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PIXE Analysis of Water Solution Using Ion Exchange Filter

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The PIXE analysis of water solution is discussed. For preconcentration of ions in water the ion exchange filter (Expapier-F2) was used and the detection limit of 1ppb~5ppb for transition metals of atomic number of 22~30 was obtained. At quantitative analysis yttrium was added to the sample solution as an internal standard. Samples analysed in the experiments were drinking water, wine, fruit juice etc., and ions detected were mainly Fe, Zn, Cu and Pb.

KEY WORDS: PIXE analysis/ ion exchange filter/ quantitative analysis/

I. INTRODUCTION

PIXE (Proton Induced X-ray Emission) is an extremely sensitive and multielemental analytical method and have been applied to various fields recently.¹⁾ We have been analysing many kinds of samples by the external beam method using Kyoto University Cyclotron.²⁾ At routine analysis it is required that data are taken efficiently and preparation of samples is easy. For these purposes we used an automatic sample changing system in helium atmosphere and prepared samples by preconcentration using the ion exchange filter. The method using the ion exchange filter was applied on PIXE and X-ray fluorescent analysis by others previously.^{1), 3), 4), 5)} Although they used filter paper in which ion exchange resin was loaded, we used expapier-F2 filter of fibers which have chelating functional groups. The expapier-F2 filter has better performances than the others in the filtration speed, the collection capacity and so on.

II. EXPERIMENTAL

A. Apparatus

Figure 1 shows the experimental set up of the PIXE experiment. The proton beam from Kyoto University Cyclotron passed through an energy degrader (aluminum foil) and a titanium window foil of 6.67 mg/cm² thickness, and went ahead straight 90cm to a target in helium gas. It was possible to select the proton energy from 7 MeV to 2 MeV by changing the thickness of the energy degrader remotely. We used the degrader of 35.76 mg/cm² thickness and got 4.2 MeV proton beam. At this energy a maximum signal to background ratio was obtained. In front of the target a graphite collimator was put to collimate the beam to get a spot of about 15 mm diameter. We used an automatic sample changer which was rebuilding of a commercial slide projector, and

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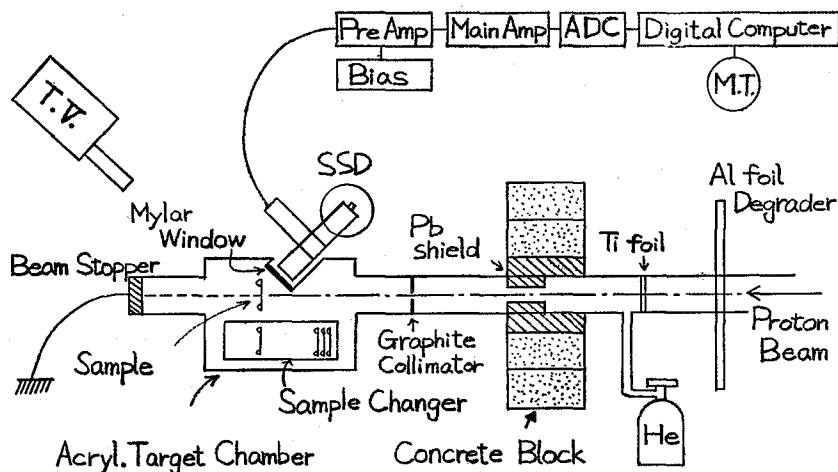


Fig. 1. Experimental set up of PIXE analysis by external beam method.

used slide mounts as sample holders. Thirty six samples could be analysed at one time.

A beam duct and a target chamber were made of acrylic resin for suppressing the production of X-ray by scattered protons and background γ -rays. The target chamber was filled with helium gas at atmospheric pressure, on this occasion sample changing became easier and some other advantages were obtained in experiments.²⁾

Lead blocks and concrete blocks were put around the energy degrader and the graphite collimator to shield the background γ -rays. A cylindrical lead block which had a central beam hole was put inside the beam duct to shield the γ -rays which were scattered forward at the energy degrader, the window foil and others. From the background consideration, the X-ray from the sample was detected at backward direction to the proton beam. A pure-Ge X-ray detector was set at a position of 6 cm from the target and at direction of 135° to the beam line. X-rays from the target passed through the thin mylar window foil were detected by the detector. Electronics for pulse height measurements were shown in Fig. 1. The pulse height data were recorded in magnetic tapes and the energy and the area of peaks were calculated by an automatic γ -ray analysis program using YHP 2100 computer. The FWHM value for total PIXE system was 220 eV at 6.4 keV X-ray and the detectable energy limit was 2,622 keV (Cl-K α).

B. Procedure of Experiment

Expapier-F2 ion exchange filters were obtained from Sumitomo Chemical Co. Ltd.. The filter was constituted by fibers which had chelating minodiacetate functional groups. Since the chelating filter works optimally in the neutral pH range, additional pH adjustment which might introduce contamination of the sample was not required usually for natural water samples. The filter collects heavy metal ions more selectively than usual acid ion exchange resin when alkali or alkaline earth ions present. The filter had 25 mm diameter, 2 cm² effective area of filtration and 18 mg/cm² weight. The procedure of sample preparation is as follows and the flow chart is shown in Fig. 2.

1. Passing the acid (2N HCl 10ml) through the filter by an aspirator to remove the impurity metals in the filter.

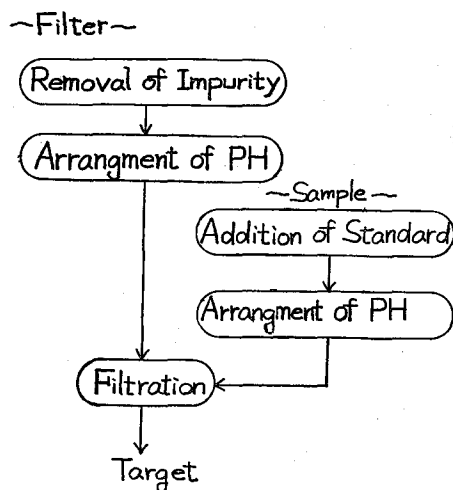


Fig. 2. Flow chart of preparation procedure of expapier-F2 ion exchange filter.

2. Pouring the buffer solution (1N CH_3COOH -1N CH_3COONa pH6.5) to the filter to arrange pH.
3. Adding the yttrium standard to the sample solution and arranging pH by 1N NH_4OH or 1N CH_3COOH .
4. Filtration of the sample solution by the aspirator.
5. Drying the filter.
6. Putting the filter on the commercial slide mount.
7. Irradiation the filter by proton beam.

The yttrium standard was made by dissolving Y_2O_3 in dilute HCl. The standard solution of other metals were dilution of the standard solution for atomic absorption spectrochemical analysis by pure water.

III. SENSITIVITY CALIBRATION

A. Blank sample

Fig. 3 shows the X-ray spectrum of the blank filter and Fig. 4 shows that of the filter which 100 cc pure water passed through. It was found that the blank filter contained Ca, Fe, Zn and Cu as an impurity and that these impurities can be removed by filtration of acid. Cl and Fe peak at the spectrum in Fig. 4 were due to contaminations in pure water. Fe could not be eliminated throughout the experiment.

B. PH and temperature

25 ml of solutions of various pH levels containing 1ppm of Co^{2+} and Zn^{2+} and 4 ppm of Y^{3+} were passed through a Expapier-filter and collection yield were measured. As expected, lowering of the collection yield was found at the lower pH level. As the optimal pH range for filtration was considered to be neutral, all following experiments were carried out at almost neutral pH level.

Similarly collection yields at various solution temperature were measured up to 40°C for 25 ml of 1ppm Cu^{2+} and Zn^{2+} . Results were shown in Fig. 5. Although the collection yield became slightly larger above 30°C , temperature could not be a significant

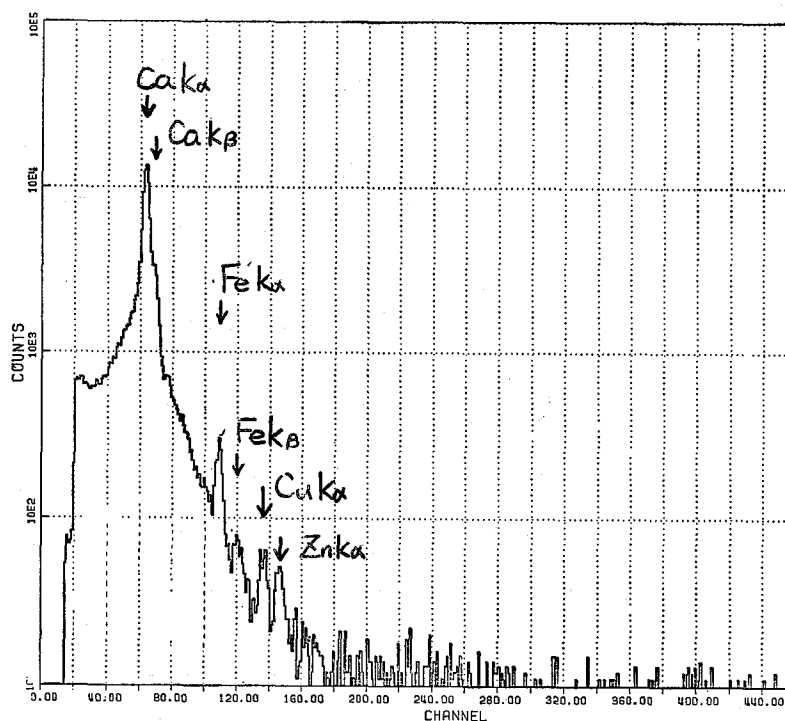


Fig. 3. X-ray spectrum of impurities contained in blank Expapier-F2 filter. Sample was bombarded with protons of 4.2 MeV.

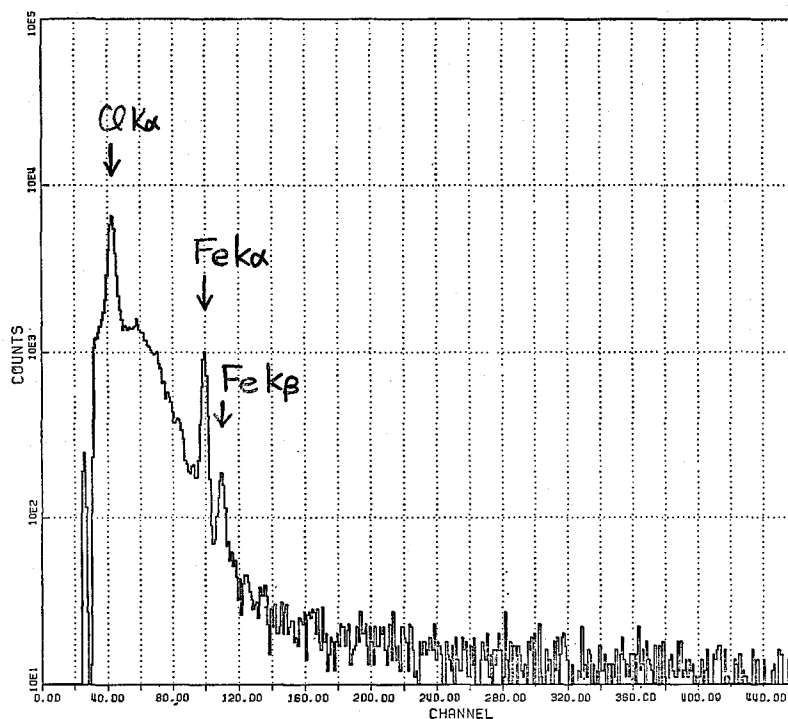


Fig. 4. X-ray spectrum of filter when 100cc pure water was passed through. Sample was bombarded with protons of 4.2 MeV.

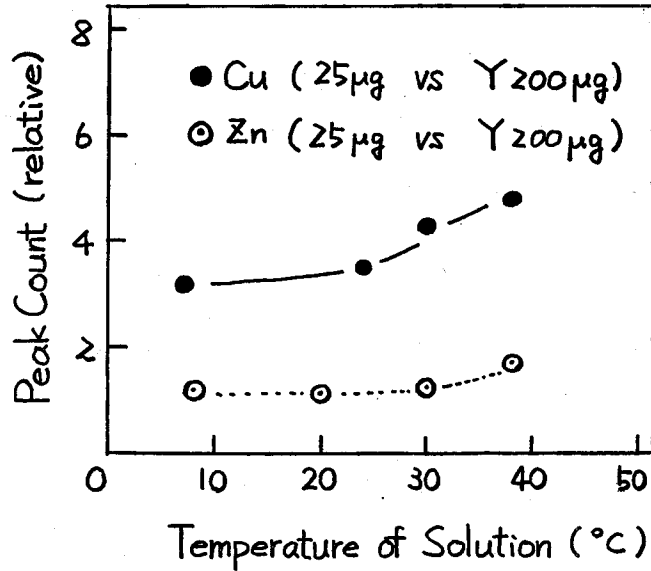


Fig. 5. Temperature dependence of ion collection yield by Exparier-F2 filter (● : Cu 25µg, ○ : Zn 25µg, standard Y 200µg)

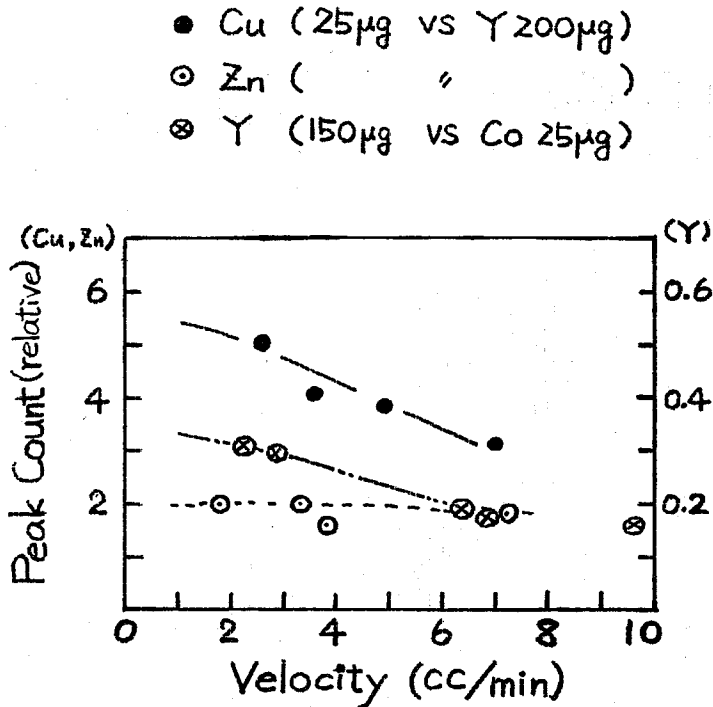


Fig. 6. Filtration speed dependence of ion collection yields. ● : Cu 25µg, standard Y 200µg, ○ : Zn 25µg, standard Y 200µg, ⊗ : Y 150µg, standard Co 25µg.

parameter on usual experiments.

C. Filtration speed

25 ml of 1ppm solutions of Cu^{2+} and Zn^{2+} and 30 ml of 5ppm Y^{3+} solutions were filtered at the speed of 2cc/min~10cc/min, and the result were shown in Fig. 6. When 25 ml of 1ppm Cu^{2+} solutions were passed through a stack of Expaper F21 filter at the speed of 2.8cc/min and 5cc/min, almost perfect recovery of Cu^{2+} was achieved by a stack of more than three filters in each case. The collection yields of the first filter were about 90% and 65% respectively. It followed from these fact that the major

Table I. Reproducibility of peak count ratio of Cu and Zn in X-ray spectrum. 25 ml of 1ppm solutions of Cu^{2+} and Zn^{2+} were passed through the filter.

	Cu $K\alpha$ / Y $K\alpha$	Zn $K\alpha$ / Y $K\alpha$
1	2.576 ± 0.055	1.152 ± 0.025
2	3.694 ± 0.077	1.062 ± 0.026
3	3.316 ± 0.070	1.344 ± 0.027
4	3.151 ± 0.057	1.362 ± 0.036
5	3.286 ± 0.060	1.295 ± 0.027
	3.205 ± 0.029	1.243 ± 0.013

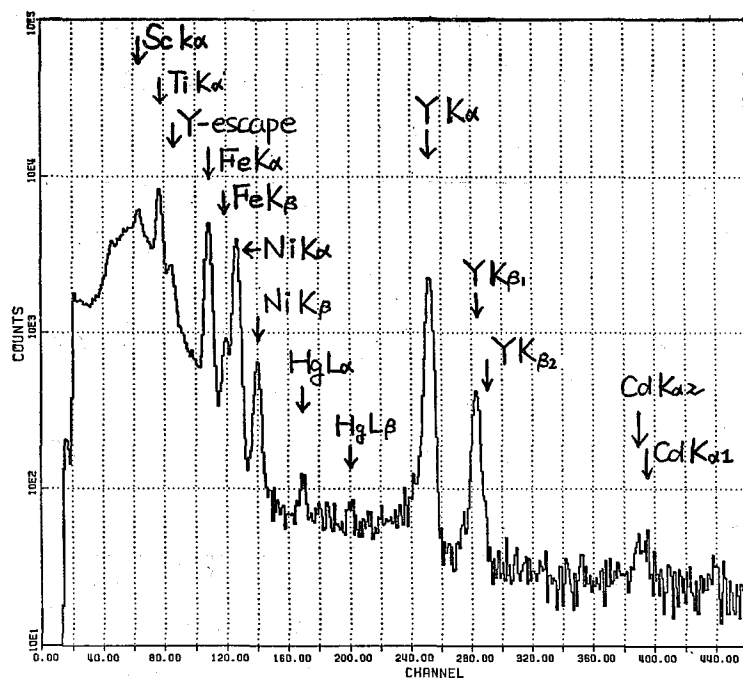


Fig. 7. X-ray spectrum of Group 1 by bombardment with proton of 4.2 MeV. Ti, Fe, Ni, Co and Hg of 50 μg respectively was passed through the filter.

portion of ions in the solution could be collected by single filter at the filtration speed of 3cc/min.

D. Reproducibility

25 ml of 1ppm solutions of Cu^{2+} and Zn^{2+} containing 200 μg yttrium as standard were passed through the filter and the reproducibility of peak count in X-ray spectrum was examined. The results was shown in Table I. The standard deviations of five measurements were 12.6% for Cu^{2+} and 10.5% for Zn^{2+} . The value could become smaller when filtration was done more carefully and more skillfully.

E. Sensitivity calibration

Standard solutions containing several kinds of metals with the content ranging 0.01 μg to 1 mg were prepared by diluting the standard solutions for atomic absorption spectrochemical analysis by pure water. After the filtration, the proportionality between the count of peak in X-ray spectrum and the weight of metal was examined.

Thirteen kinds of metal ions were divided into three groups as follows and the proportionality was examined.

Group 1. Ti, Fe, Ni, Cd, Hg

Group 2. Mn, Co, Cu, Sn

Group 3. Zn, Sr, Ag, Pb.

The examples of measured spectra are shown in Figs. 7, 8 and 9. As for Ag, Cd, Sn and Hg, the measured proportionality was not so good. We thought that this would be

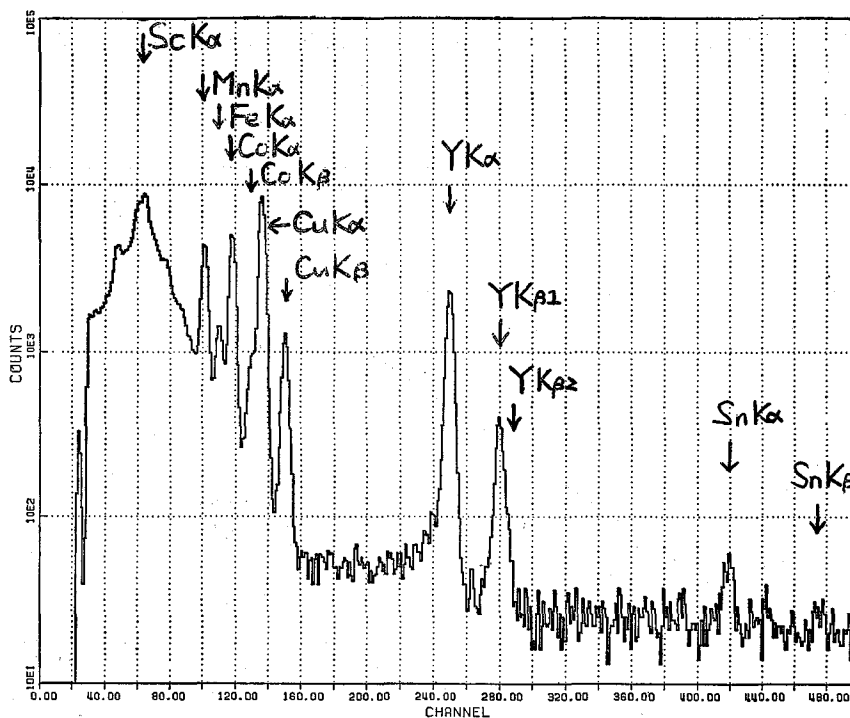


Fig. 8. X-ray spectrum of Group 2, bombarding condition was same as Fig. 7, Mn, Co, Cu and Sn of 50 μg .

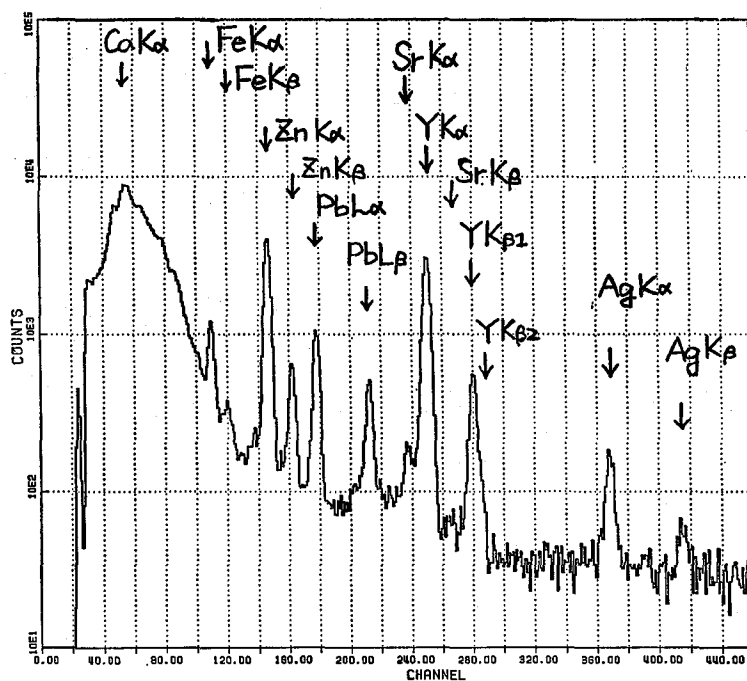


Fig. 9. X-ray spectrum of Group 3, bombarding condition was same as fig. 7, Zn, Sr, Ag and Pb of 50 μ g.

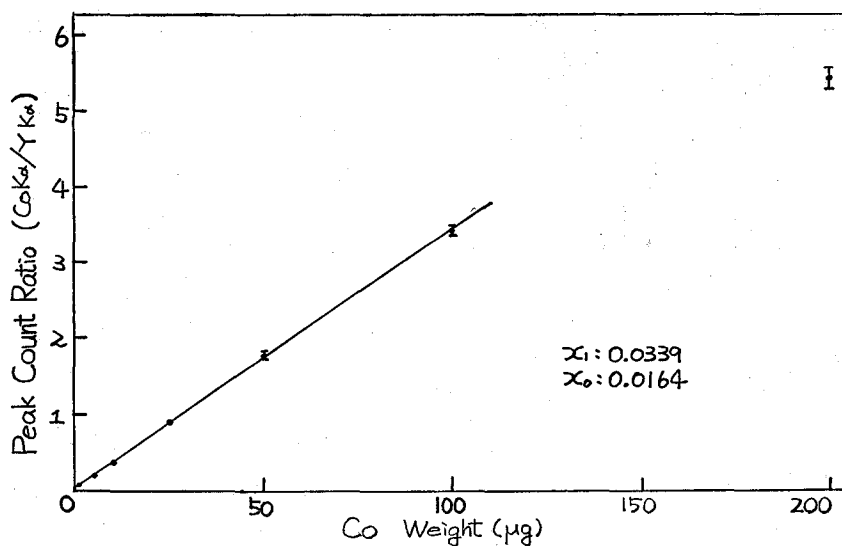


Fig. 10. Relative sensitivity of Co K α X-ray to yttrium K α X-ray, 500 μ g yttrium was added as an internal standard.

PIXE Analysis of Water Solution Using Ion Exchange Filter

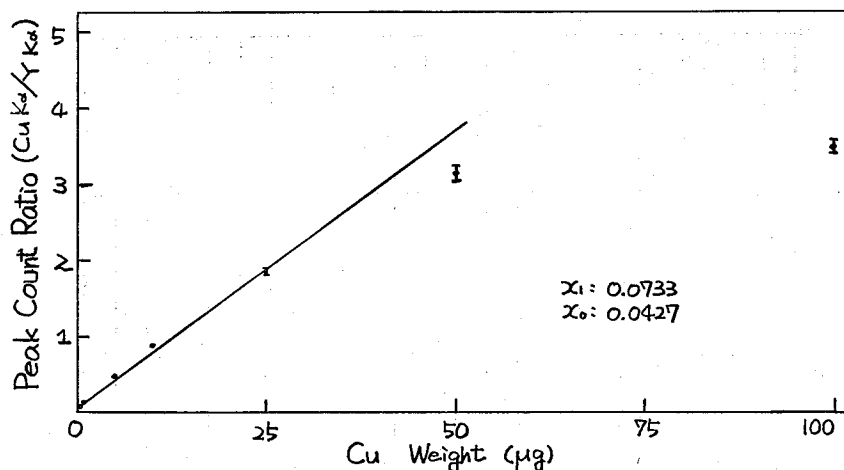


Fig. 11. Relative sensitivity of Cu K α X-ray, experimental condition was same as Fig. 10.

Table II. Lowest detecting limit of metal in the solution. Irradiation time was 15 minutes.

element	atomic number	limit (μ g)	element	atomic number	limit (μ g)
Ti	22	0.1	Sr	38	5
Mn	25	1	Ag	47	25
Fe	26	0.1	Cd	48	25
Co	27	1	Sn	50	50
Ni	28	5	Hg	80	25
Cu	29	0.5	Pb	82	5
Zn	30	0.5			

due to the lower filtration efficiency for these metals.

The results for Co and Cu were plotted in Figs. 10 and 11. The deviations from the linearity at the larger weight were due to the saturation of the capacity of the filter. Table II shows the lower limit of the detection for each metal.

IV. RESULTS

A. Drinking water

Fig. 12 shows the spectrum for the 100 ml of city water. Ca, Ti, Mn, Fe Cu, Zn, Pb and Sr were detected. Rickey *et al.*³⁾ had detected also Se, Br, Mn, Cd and Ba in the drinking water, but we could not detect these ions. The calibrated concentrations of some ions from the measurements were shown in Table III.

B. Alcoholic drink and fruit juice

We chose wine and fruit juice as samples because of their richness of trace metal elements which originated from chemical manure and agricultural medicine. Table IV shows the result and some examples of measured spectra were shown in Figs. 13, 14 and 15.

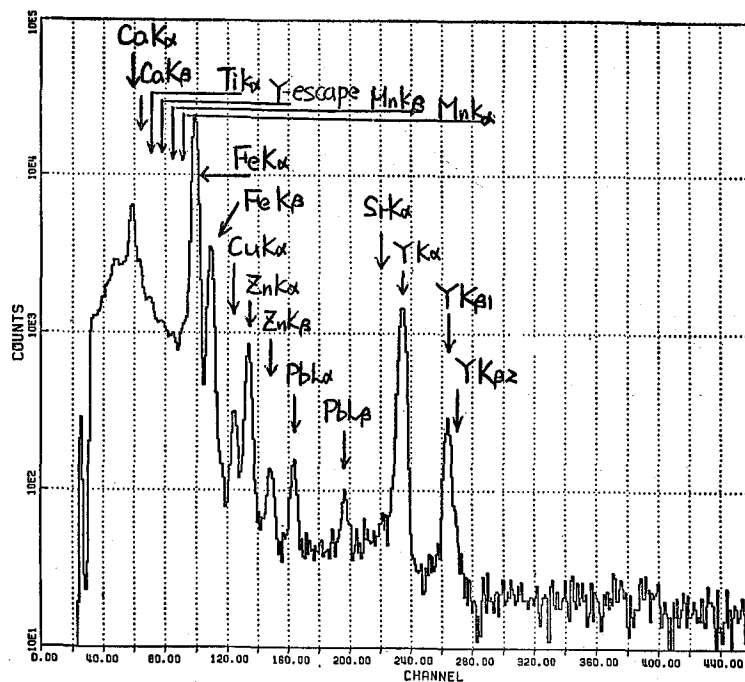


Fig. 12. X-ray spectrum of Expapier-F2 filters passed through drinking water of 100 cc by bombardment with protons of 4.2 MeV.

Table III. Metal contents of drinking water.

	concentration (ppm)
Mn	0.11
Fe	~5
Cu	0.015
Zn	0.18
Pb	0.11

Table IV. Trace metal contents of alcoholic drink and fruit juice. 100 ml of sample was passed through the filter. In the case of beer 100 ml could not be passed through because the filter was blocked. ○ means presence of peak in X-ray spectrum is recognized.

	Mn	Fe	Ni	Cu	Zn	Pb	
sake	0.34	○	—	○	0.42	0.02	Sr
white wine	0.21	3.42	0.03	0.06	1.85	—	
rose wine	0.56	0.82	0.02	0.04	0.48	0.26	
dry vermouth	0.57	0.51	0.03	0.03	0.93	0.10	
red wine	1.14	0.67	—	0.03	1.08	○	
blue curaçao	0.003	0.09	—	0.07	0.01	○	
slow gin	0.48	1.35	—	0.09	1.20	—	
beer*	○	○	—	○	—	○	
tomato juice	0.58	0.29	0.01	0.01	0.56	—	
apple juice	0.26	0.27	—	0.05	0.13	—	
orange juice	—	0.58	—	0.006	0.34	—	
canned orange	0.58	1.45	—	—	3.62	—	Cr, Sn

PIXE Analysis of Water Solution Using Ion Exchange Filter

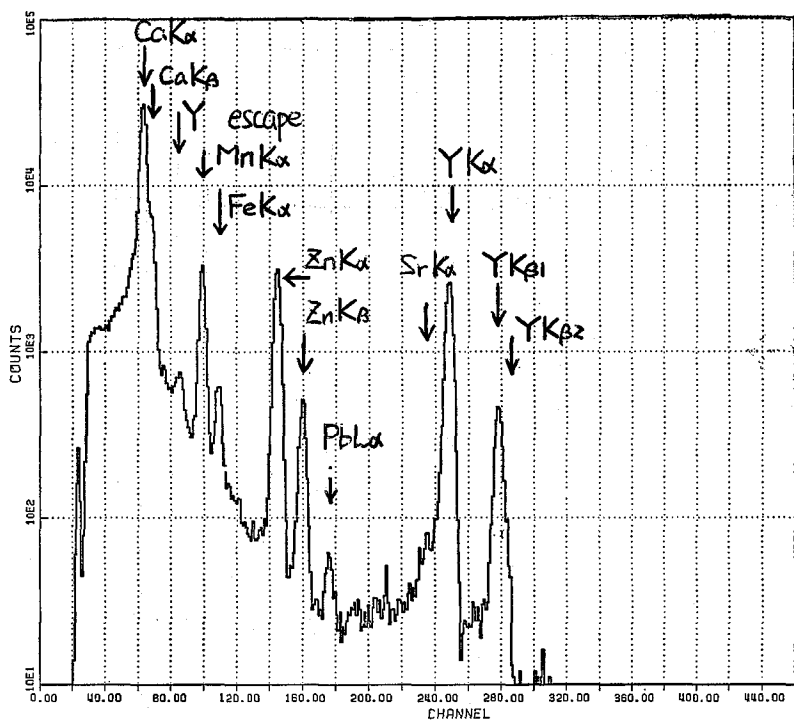


Fig. 13. X-ray spectrum of sake of 100cc, experimental condition was same as Fig. 12.

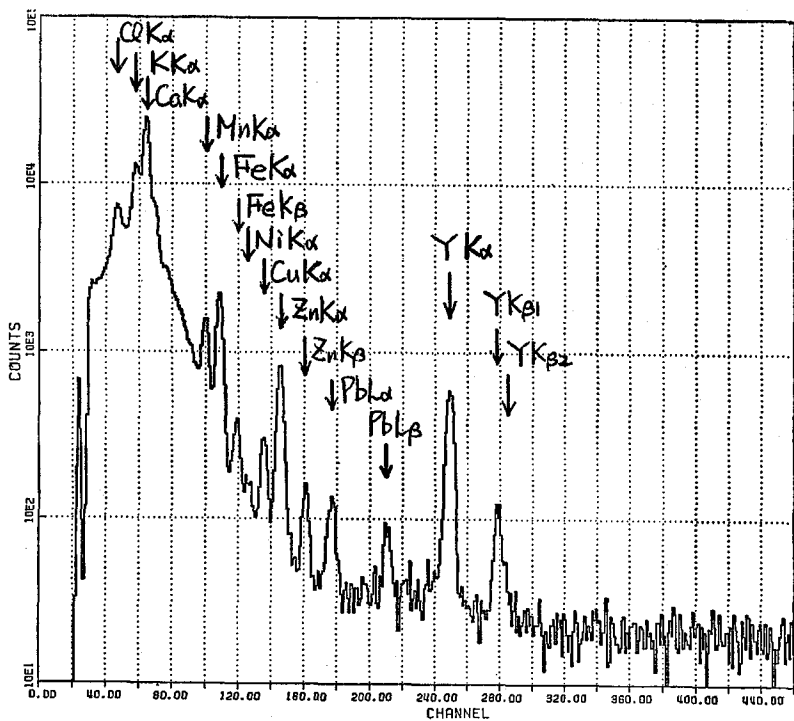


Fig. 14. X-ray spectrum of rose wine of 100cc, experimental condition was same as Fig. 12.

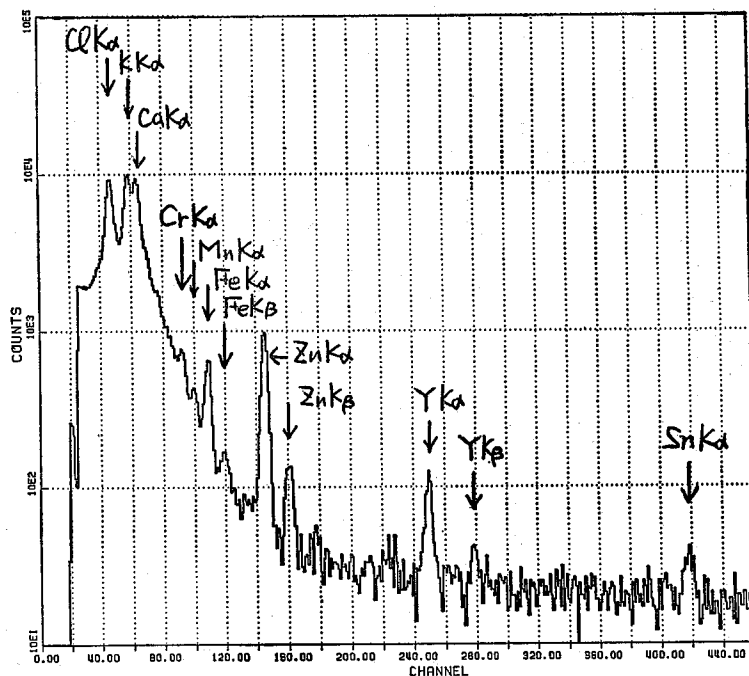


Fig. 15. X-ray spectrum of canned orange juice, experimental condition was same as Fig. 12.

V. CONCLUSION

PIXE analysis using Expapier-F2 ion exchange filter enables the trace metal element analysis of water solution with the sensitivity of 1ppb~5ppb for metals of atomic number of 20~30. At present the accuracy of the measurement is about 20%, but it would be improved great deal by further experiments.

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